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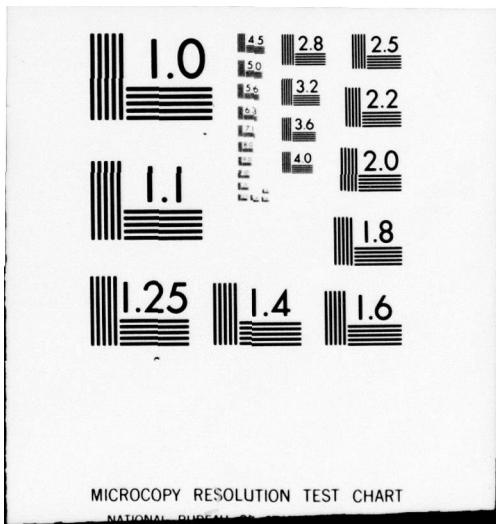
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HERBERT C. BROWN  
PRINCIPAL INVESTIGATOR

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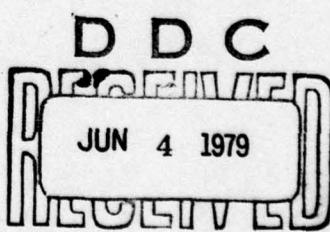
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## 20. ABSTRACT

→ Lithium triethylborohydride (Super Hydride) is a versatile reagent. It cleanly reduces alkyl tosylates to hydrocarbons, providing a convenient procedure for the deoxygenation of alcohols. Super Hydride reduces tertiary amides into primary alcohols via carbon nitrogen fission during the reduction.

A chiral trialkylborohydride, lithium *B*-isopinocampheyl-9-BBN hydride was shown to be an asymmetric reducing agent for the conversion of ketones into optically active alcohols.

During this study, methods were developed for the preparation of lithium borohydride, calcium borohydride, and borane-methyl sulfide from the readily available and economical reagent, sodium borohydride.

The chemistry of dialkylborohydrides has been studied.

The reactions of various alkali metal hydrides with representative trialkylboranes have been explored in an attempt to employ the resulting reagents for organic synthesis.

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## INTRODUCTION

Forty years ago, the author, with Professor Schlesinger, observed that diborane, a hydride, reduces aldehydes and ketones with exceptional ease. Since then, various hydride reagents have evolved for the convenient reduction of typical organic functional groups. The author's major contributions in this area have led to the alkali metal hydrides and the alkali metal borohydrides.

The discovery of sodium borohydride in 1942 and of lithium aluminum hydride in 1945 brought about a revolutionary change in the procedure utilized for the reduction of functional groups in organic chemistry. The author, with the financial assistance from ARO, has been exploring the synthesis of new hydrides, their modifications and their chemistry.

Electrophilic reducing agents, such as borane and alane, possess markedly different reducing characteristics than those of nucleophilic reducing agents, such as sodium borohydride ( $\text{NaBH}_4$ ) and lithium aluminum hydride ( $\text{LiAlH}_4$ ). Explorations in the author's laboratory have revealed means of enhancing and diminishing electrophilic or nucleophilic properties of these reagents.

These hydrides, both complex and simple, have proven to be exceedingly valuable as reducing agents. They are high energy substances with fascinating properties. With the organic chemists undertaking the synthesis of structures of increasing complexity, it is desirable to develop means of controlling the reducing power of such reagents so that a complete spectrum of such reagents would be available for selective reductions.

The author's discovery of hydroboration in 1956 has made available for the first time a wide variety of alkyl substituted boranes of unusual structures. From these, a wide variety of alkyl substituted borohydrides,  $\text{LiR}_3\text{BH}$ , have been prepared and examined as possible reagents for selective reduction. These are the most powerful and highly stereoselective reducing agents now available to organic chemists. Lithium triethylborohydride (Super Hydride), lithium tri-sec-butylborohydride, and lithium trisiamylborohydride are shown to be highly selective reagents.

It should be pointed out that continued research in this area will make available specific reagents which will enable us to reduce any specific functional group in the presence of any other functional group. With our increasing understanding in this area, it is hoped that we shall be in a position to design reducing agents to perform desired reductions--as specific as the enzymes designed by nature.

ARO has been the sole source of support for our research in this major area.

### LIST OF PARTICIPATING PERSONS

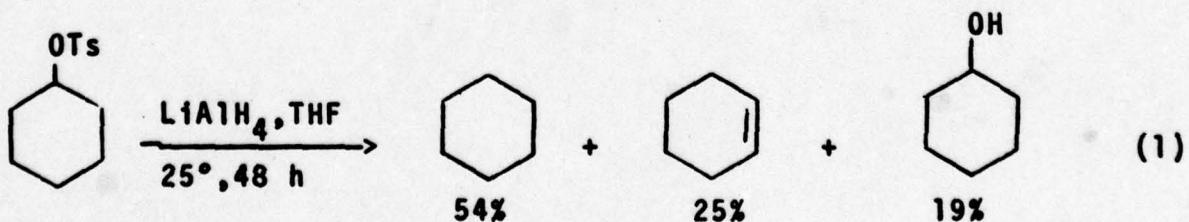
<u>Name</u>	<u>Period of Appointment</u>	<u>Nature of Appointment</u>
S. Krishnamurthy	5/1/76 - 4/25/79	Postdoctoral Research Associate
S. C. Kim	5/1/76 - 12/31/76 1/1/77 - 2/28/78	Graduate Student Postdoctoral Research Associate
J. L. Hubbard	6/1/77 - 9/1/78	Postdoctoral Research Associate
Y. M. Choi	1/1/78 - present	Postdoctoral Research Associate
P. Mathew	1/1/78 - present	Postdoctoral Research Associate

### PROBLEMS STUDIED AND THE RESULTS AND CONCLUSIONS REACHED

1. Facile Reduction of Alkyl Tosylates with Lithium Triethylborohydride.

An Advantageous Procedure for Deoxygenation of Cyclic and Acyclic Alcohols

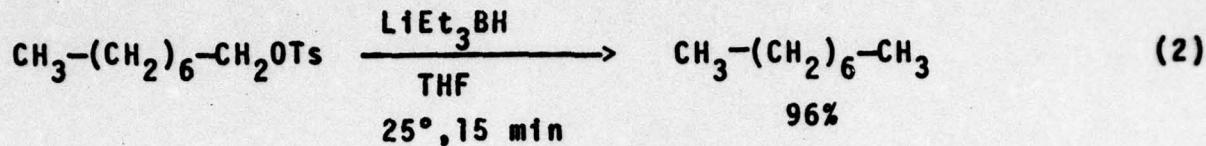
Deoxygenation of alcohols to the corresponding alkanes is usually achieved by the reduction of *p*-toluenesulfonate ester of the alcohol with lithium aluminum hydride. However, the results are less favorable for more hindered alcohols and certain cyclo-alkanols (eq 1).



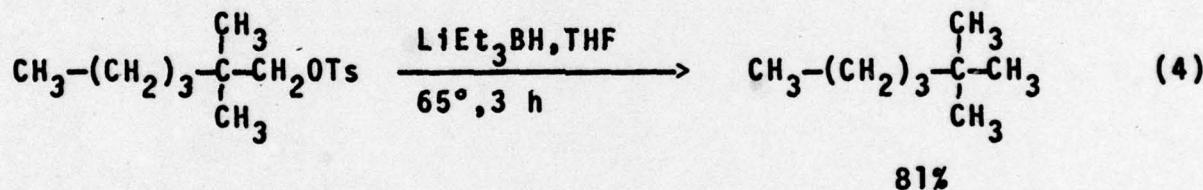
In view of the exceptional utility of lithium triethylborohydride in reducing hindered alkyl halides, epoxides and quaternary ammonium salts, it appeared possible that this reagent might overcome the difficulties.

4.

Tosylates of primary and secondary alcohols are quantitatively reduced to the corresponding hydrocarbons (eqs 2, 3).

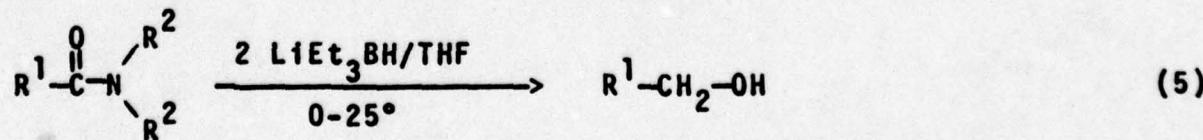


The hindered tosylates are reduced in refluxing THF providing satisfactory yield of the desired products (eq 4).



## 2. An Unusual Reduction of Tertiary Amides with Carbon-Nitrogen Fission

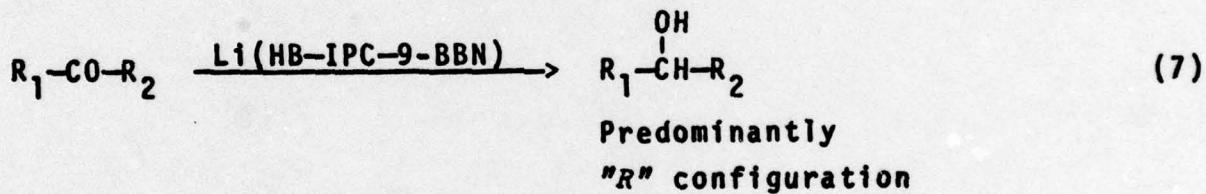
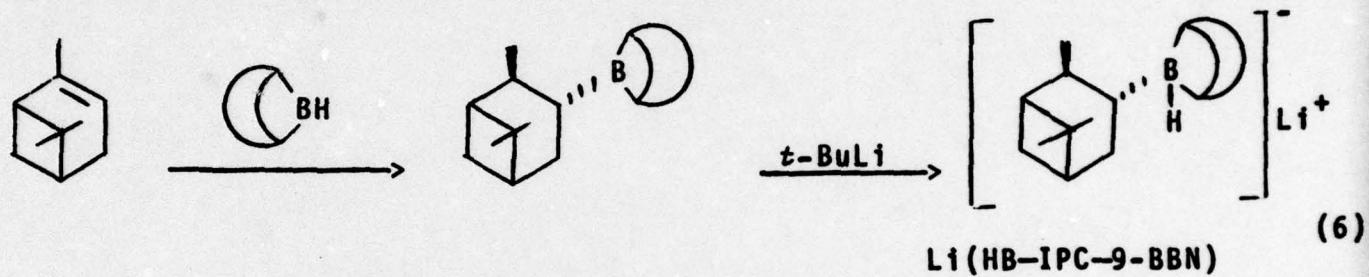
Reduction of tertiary amides with various metal hydrides or with diborane proceeds with the carbon-oxygen bond fission to give the corresponding tertiary amines. However, "Super Hydride" reduces tertiary amides to primary amines via carbon-nitrogen fission (eq 5).



This reduction proceeds presumably through the formation of aldehyde as an intermediate. A representative set of tertiary amides has been examined to show the generality of the reaction.

**3. Lithium B-Isopinocamphey-9-BBN Hydride. A New Reagent for Asymmetric Reduction of Ketones**

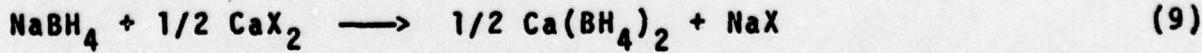
The title reagent (eq 6), a highly hindered trialkylborohydride containing an asymmetric alkyl group, reduces rapidly and quantitatively a variety of ketones to the corresponding optically active alcohols, consistently enriched in the *R* isomer (eq 7).



This reagent reduces even relatively hindered ketones rapidly and quantitatively in < 2 h at -78°C.

**4. Lithium Borohydride and Calcium Borohydride**

A synthetic procedure to prepare lithium borohydride and calcium borohydride from sodium borohydride has been studied (eq 8, 9).



Various solvents, such as isopropyl amine, monoglyme, 1,3-dioxolane, tetrahydrofuran, and diethyl ether, and various salts, such as lithium chloride, lithium bromide, lithium iodide, and calcium chloride, are

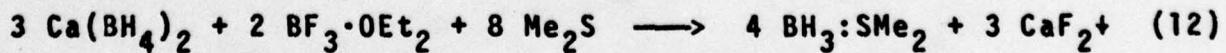
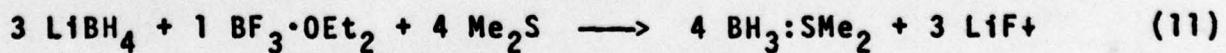
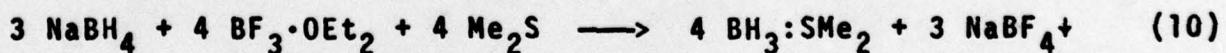
6.

used. The reactions were carried out under nitrogen atmosphere and various conditions ( $0^\circ$ ,  $25^\circ$ , and reflux temperature). A high yield (90-100%) of lithium borohydride was obtained under a certain condition. Thus, the trend of reaction is that the lithium bromide and lithium iodide reactions are much faster than lithium chloride reaction under identical conditions. For example, lithium chloride reaction in tetrahydrofuran is quite slow, producing 100% in 4 days, but lithium bromide reaction is very fast, giving 99% of lithium borohydride in 16 h under reflux temperature.

Attempts to obtain a neat lithium borohydride and calcium borohydride from solvated compound of metal borohydride [ $\text{LiBH}_4$ ,  $\text{Ca}(\text{BH}_4)_2$ ] and the solution in various solvents have been examined. A pure sample of lithium borohydride and of calcium borohydride (96-100%) were isolated under high temperature ( $100-150^\circ$ ) and vacuum ( $\sim 1 \text{ mm Hg}$ ).

##### 5. Borane-Methyl Sulfide

A synthetic procedure to develop a convenient laboratory method for the preparation of borane methyl sulfide has been investigated by reacting various borohydrides and boron trifluoride ethyl ethers (eq 10-12).

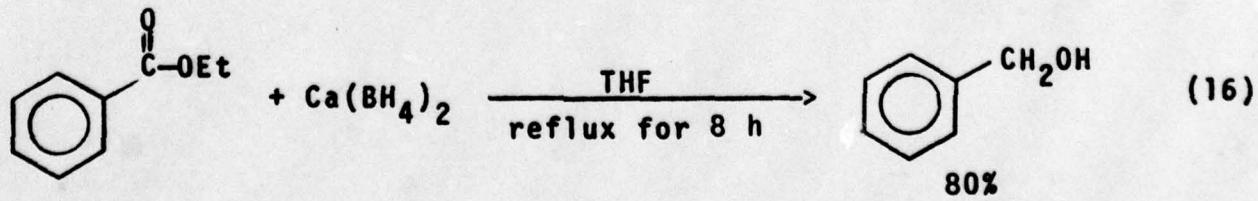
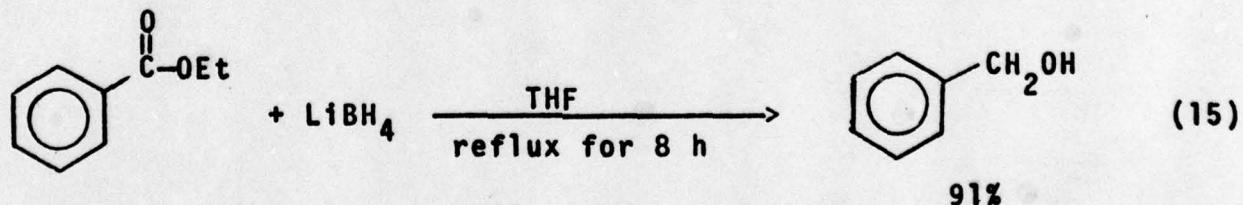
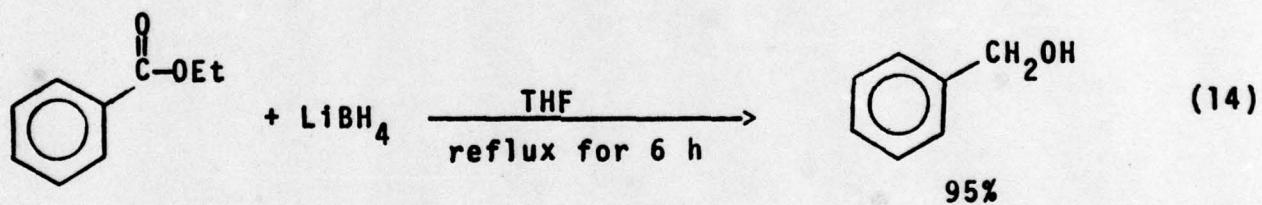
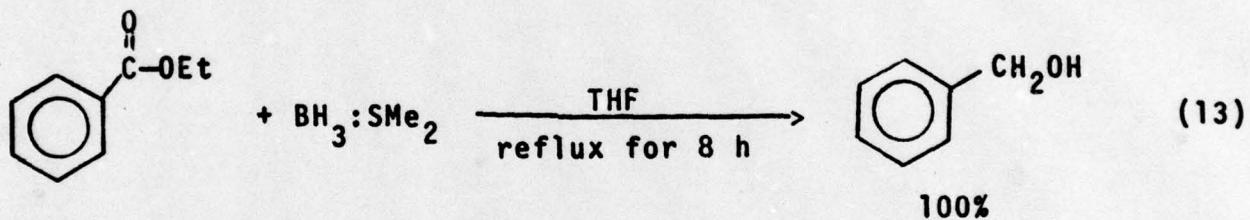


Various metal borohydrides, such as sodium borohydride, lithium borohydride, and calcium borohydride, and various solvents, 1,3-dioxolane-

dimethyl sulfide, tetrahydrofuran-dimethyl sulfide, and diethylether-dimethyl sulfide, are used. The reactions were carried out under 25° and reflux temperature. An essential quantitative yield of borane methyl sulfide was obtained from the reaction in the solvents mentioned above, except 1,3-dioxalane-dimethyl sulfide.

#### 6. Reduction of Ester

A reduction of ethyl benzoate, with the smallest reactivity among the esters, with various reducing agents, such as lithium borohydride, calcium borohydride, and borane methyl sulfide, has been studied (eq 13-16).



The reaction of borane methyl sulfide in THF and of lithium boro-hydride in monoglyme were faster than that of lithium borohydride in THF and of calcium borohydride in THF. Thus the reaction gave 100% yield of benzyl alcohol in 8 h with borane-methyl sulfide, 95% yield in 6 h with lithium borohydride in monoglyme, 91% yield in 8 h, and 80% yield of benzyl alcohol in 8 h with calcium borohydride in THF.

The reduction agent, borane-methyl sulfide, in tetrahydrofuran will be very useful agent in reduction of any ester in organic compound, but without an internal and terminal double bond. Alternatively, lithium borohydride in monoglyme would like to be reacted with any ester in organic compound.

#### 7. Selective Reductions of Functional Groups in Organic Compound Using Various Super Hydrides

Selective reductions of various organic compounds with representative trialkylborohydrides have been studied.

Various super hydrides, such as  $\text{LiBH}_3\text{-Bu}_3$ ,  $\text{LiBHSi}_3$ ,  $\text{KBH}_3\text{-Si}_3$ ,  $\text{KBHEt}_3$ , and  $\text{KBH}(i\text{-PrO})_3$  and ten compounds, such as cyclohexanol, 3-ethyl-3-pentanol, cyclohexanone,  $\alpha,\beta$ -unsaturated cyclohexanone, *n*-octyl bromide, benzonitrile, *N,N*-dimethyl benzamide, styrene oxide, benzoyl chloride, and ethyl benzoate, are used. The stoichiometric reactions were carried out under nitrogen atmosphere and 0° in both tetrahydrofuran and toluene.

#### 8. Reaction of Mono- and Dialkylboranes with Lithium, Sodium and Potassium Hydrides

Hydroboration studies have made available a number of mono- and dialkylboranes exhibiting unique reducing characteristics. It was

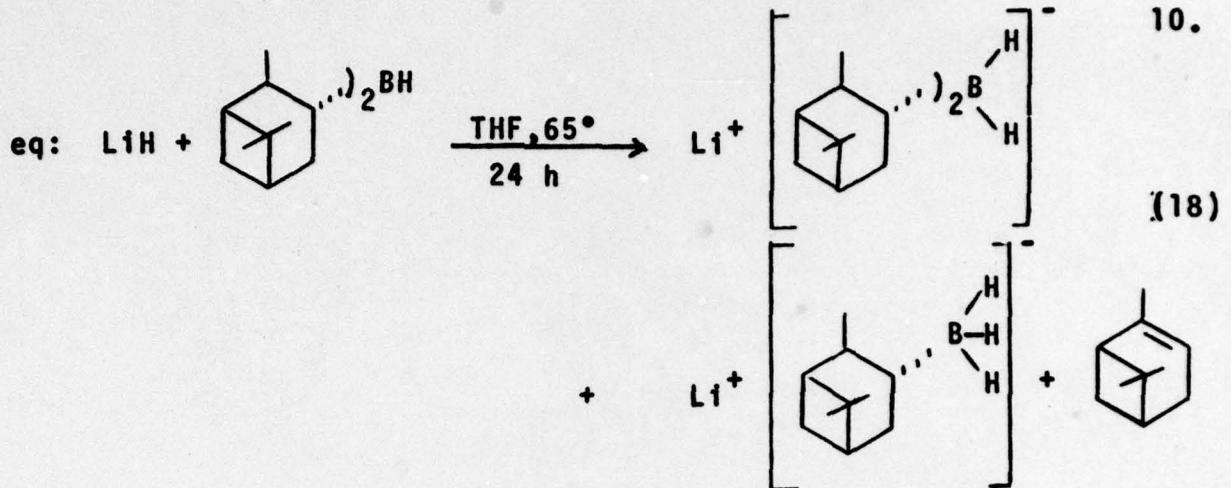
felt that the corresponding alkali metal borohydrides might show interesting hydride transfer ability in reductions. Accordingly, a systematic study was undertaken on the reaction of lithium, sodium and potassium hydrides with mono- and dialkylboranes.

The following alkylboranes were selected for this study: the hexylborane ( $\text{THBH}_2$ ), monoisopinocampheylborane ( $\text{IPCBH}_2$ ), 9-borabicyclo-[3.3.1]nonane (9-BBN), dicyclohexylborane [ $(\text{CH}_2)_2\text{BH}$ ], and diisopinocampheylborane [ $(\text{IPC})_2\text{BH}$ ]. In general, the reactions were carried out by vigorously stirring a 0.5 M solution of the alkylborane in THF with a slight excess of the metal hydride (~ 50%) at room temperature.

$\text{LiH}$  reacted with 9-BBN and  $\text{THBH}_2$  at room temperature requiring 48 h for completion (eq 17).

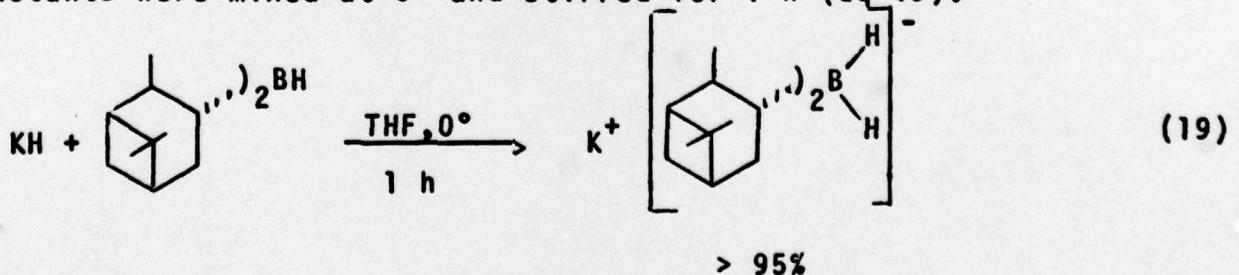


The other alkylboranes were almost inert to  $\text{LiH}$  under these conditions. In all cases there was an inductive period of 6-8 h before  $\text{LiH}$  started reacting. Consequently, the reactions were repeated in refluxing THF. It was observed that  $\text{Li}^+ \left[ \text{C}_6\text{BH}_2 \right]^-$  and  $\text{Li}^+ \left[ \text{ThBH}_3 \right]^-$  were formed in 100% yield within 3 h. However, this procedure was unsuitable for preparing the other borohydrides. Unlike 9-BBN and  $\text{THBH}_2$ , the other alkylboranes are not thermally stable and therefore underwent redistribution and/or elimination (eq 18).



The reaction of organoboranes with sodium hydride is far more facile than the corresponding reactions involving lithium hydride. Even hindered dialkylboranes, such as  $(\text{IPC})_2\text{BH}$ , reacted quantitatively with sodium hydride at  $25^\circ$ .

Finally, potassium hydride reacted almost instantly and quantitatively with all the alkylboranes used in this study. Reactions were so rapid and vigorous that care was needed to control the reaction by cooling the reaction flask in a water bath ( $20^\circ$ ). However, the reaction with  $(\text{IPC})_2\text{BH}$  is so vigorous that it undergoes dehydroboration up to 20%. In order to minimize this side reaction, the reactants were mixed at  $0^\circ$  and stirred for 1 h (eq 19).



11.

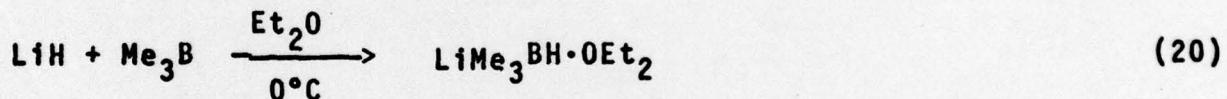
9. Reaction of Lithium 9-Borabicyclo[3.3.1]nonane Hydride,  $\text{Li}^+ \left[ \begin{array}{c} \text{C} \\ \diagup \\ \text{B} \\ \diagdown \\ \text{H} \end{array} \right]^-$ , with Selected Organic Compounds Containing Representative Functional Groups

The reducing property of  $\text{Li}^+ \left[ \begin{array}{c} \text{C} \\ \diagup \\ \text{B} \\ \diagdown \\ \text{H} \end{array} \right]^-$  was explored by reacting

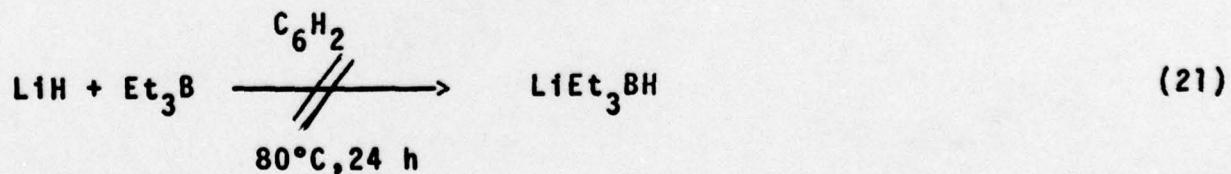
it with selected organic compounds containing representative functional groups.

10. Reactions of Alkali Metal Hydrides with Trialkylboranes

Lithium hydride reacts with trimethyl- and triethylborane in ethereal solvents to give the corresponding lithium trialkylborohydrides as monoetherates (eq 20).



Removal of the solvent from the monoetherate adduct is possible leaving behind the solvent-free alkali metal trialkylborohydride. However, in the absence of ether, lithium trialkylborohydride is not formed (eq 21).



These complex borohydrides can be reversibly decomposed by heating to yield "activated" lithium hydride and trialkylborane.

In contrast, sodium hydride reacts with trialkylboranes in the absence of solvents, yielding sodium trialkylborohydrides. The

corresponding reactions with commercial lithium hydride do not proceed. However, the activated lithium hydride does react with trialkylboranes in the absence of solvents to form unsolvated  $\text{LiR}_3\text{BH}$ .

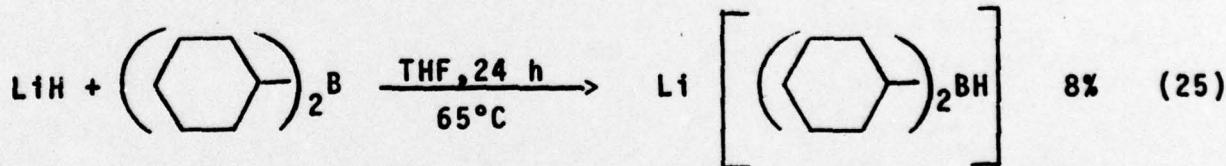
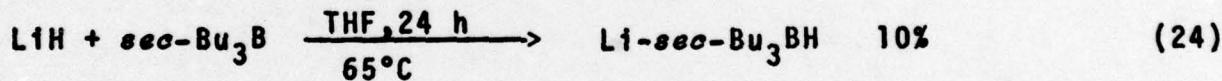
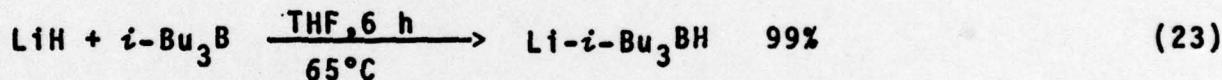
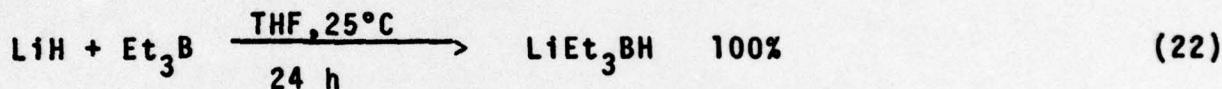
Thus, a mixture of trialkylborane and ether can be considered as a reversible solvent for lithium hydride, permitting its solution and recovery in active form.

### 11. The Reaction of Trialkylboranes with Lithium Trialkylborohydrides

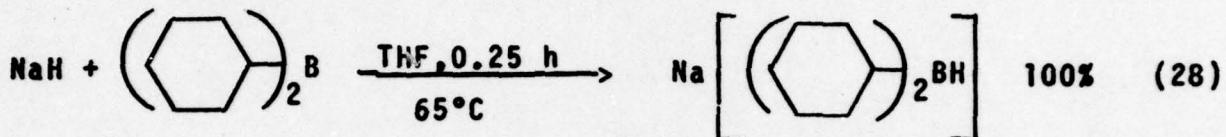
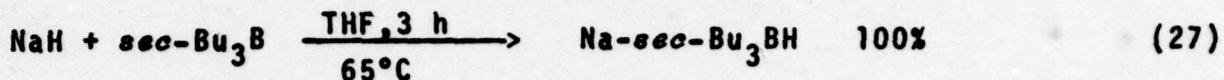
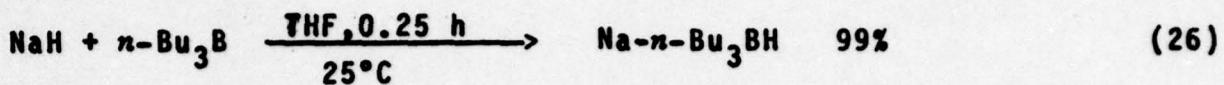
Lithium hydride reacts with trimethylborane in solvents such as ethyl ether, *n*-butyl ether, etc., to form lithium trimethylborohydride (1:1 adduct,  $\text{LiMe}_3\text{BH}$ ). Further addition of trimethylborane does not result in the formation of lithium hexamethyldiborohydride (1:2 adduct,  $\text{LiMe}_3\text{BHBMe}_3$ ). However, in solvents such as tetrahydrofuran, monoglyme, diglyme, etc., the corresponding reaction gives either lithium trimethylborohydride or lithium hexamethyldiborohydride, depending upon the amount of trimethylborane. The following explanation nicely accounts for this major effect of solvent upon the reaction course. In solvents, such as ethyl ether, which are relatively poor solvating media for the lithium ion, the borohydride anion must be strongly associated with the lithium ion and is thus not free to add the additional trialkylborane. However, in solvents such as tetrahydrofuran, which solvate lithium ion strongly, the association is much weaker if it occurs at all. Then borohydride anions are relatively free to interact with trialkylboranes to form 1:2 addition compounds. The rates of reductions of alkyl halides with lithium triethylborohydride in various solvents, together with infrared and  $^{11}\text{B}$  NMR studies, strongly support the above results and interpretations.

**12. Steric Effects in the Reaction of Representative Trialkylboranes with Lithium and Sodium Hydrides**

The reaction in tetrahydrofuran of lithium and sodium hydrides with representative trialkylboranes of increasing steric requirements was examined in detail with respect to rate, stoichiometry, and products. The rate of the reaction is strongly influenced by the steric requirements of the trialkylboranes. Thus, the rates of reaction of lithium hydride with a series of trialkylboranes at 25°C follows the order  $\text{Et}_3\text{B} > n\text{-Bu}_3\text{B} > i\text{-Bu}_3\text{B} \gg \text{sec-Bu}_3\text{B}$  (eq 22-25).



Even in refluxing tetrahydrofuran, tri-*sec*-butylborane and other hindered organoboranes react with lithium hydride sluggishly and incompletely. Sodium hydride exhibits greater reactivity than lithium hydride in these reactions. Sodium hydride reacts with essentially all of the unhindered trialkylboranes and with a number of hindered trialkylboranes even at 25°C (eq 26-28).

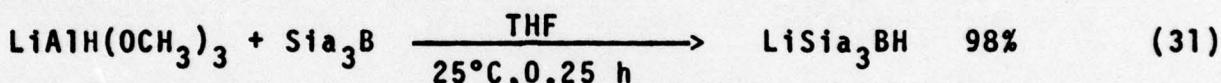
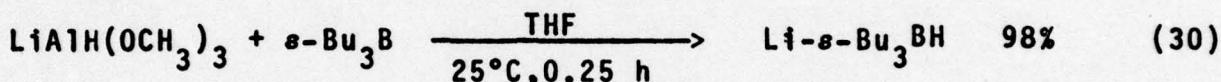
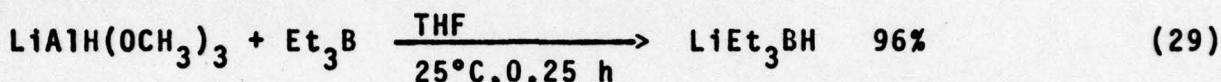


Other hindered trialkylboranes, such as tri-*sec*-butylborane, tricyclohexylborane, and tri-*exo*-2-norbornylborane, react with sodium hydride in refluxing tetrahydrofuran rapidly and quantitatively. Here again the rate of the reaction decreases drastically with increasing size of the alkyl substituent on boron:  $\text{Et}_3\text{B} > n\text{-Bu}_3\text{B} >$  tricyclopentylborane  $\geq$  *i*- $\text{Bu}_3\text{B} >$  tricyclohexylborane  $\geq$  tri-*exo*-2-norbornylborane  $\geq$  *sec*- $\text{Bu}_3\text{B}$ . Highly hindered organoboranes, such as trisiamylborane and tris(*trans*-2-methylcyclopentyl)borane, are essentially inert toward both lithium hydride and sodium hydride at 65°C. The reaction of alkali metal hydrides with trialkylboranes proceeds in 1:1 stoichiometry; the products of the reaction are alkali metal trialkylborohydrides characterized by hydride analysis, IR, and  $^{11}\text{B}$  NMR. The present reaction serves as a convenient means for studying the steric requirements of various trialkylboranes. In addition, it also provides a simple route to a number of lithium and sodium trialkylborohydrides.

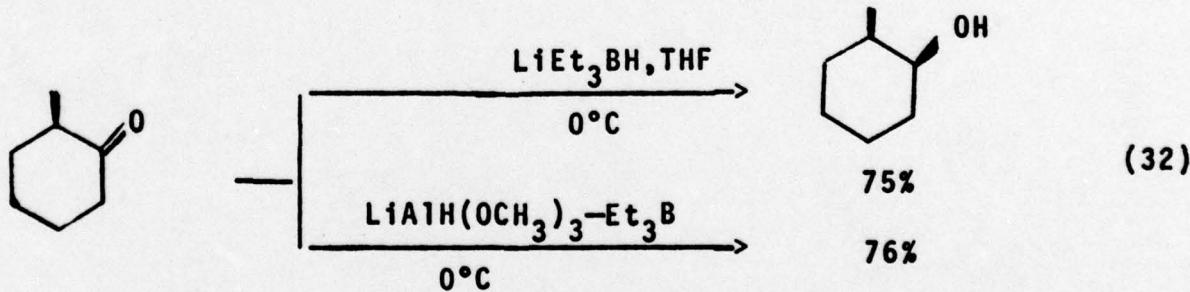
### 13. Facile Reaction of Trialkylboranes with Lithium Trimethoxyaluminohydride

Addition of one mole equivalent of trialkylborane to a tetrahydrofuran (THF) solution of lithium trimethoxyaluminohydride (LTMA)

at room temperature results in a facile and rapid displacement of aluminum methoxide as a polymeric gel, producing the corresponding lithium trialkylborohydride in quantitative yield. The reaction is quite general and applicable to trialkylboranes of widely varied structural requirements (eq 29-31).



The trialkylborohydrides thus produced can be directly utilized for the stereoselective reduction of organic functional groups without the necessity of removing aluminum methoxide (eq 32).

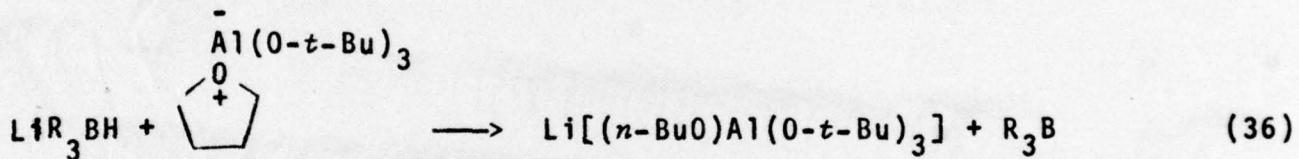
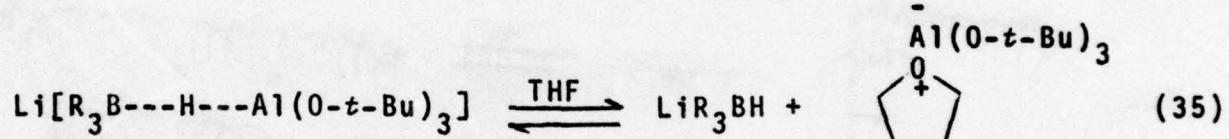


The present reaction provides a general, convenient *in situ* synthesis of lithium trialkylborohydrides where this is required in synthetic transformations.

#### 14. An Unusual Reaction of Trialkylboranes with Lithium Tri-*n*-butoxyaluminohydride in Tetrahydrofuran

Addition of equimolar or catalytic quantities of trialkylboranes to a tetrahydrofuran solution of lithium tri-*t*-butoxyaluminohydride

results in rapid loss of active hydride with the concurrent formation of 1-butanol (from the reductive cleavage of tetrahydrofuran). The rate of reductive cleavage decreases with increasing steric requirements of the trialkylborane (eq 33-36).



In contrast to the tetrahydrofuran, tetrahydropyran is cleaved sluggishly. Consequently, this solvent can be utilized to follow the course of the reaction of lithium tri-*t*-butoxyaluminohydride with representative trialkylboranes by  $^{11}\text{B}$  NMR. Chemical and spectral evidence suggest the intermediacy of lithium trialkylborohydrides and aluminum-*t*-butoxide in these reactions.

**LIST OF PUBLICATIONS**  
**(In the Order of Date of Publication)**

1. Facile Reduction of Alkyl Tosylates with Lithium Triethylborohydride. An Advantageous Procedure for Deoxygenation of Cyclic and Acyclic Alcohols  
 S. Krishnamurthy and H. C. Brown  
*J. Org. Chem.*, 41, 3064 (1976)
2. An Unusual Reduction of Tertiary Amides with Carbon-Nitrogen Fission  
 H. C. Brown and S. C. Kim  
*Synthesis*, 635 (1977)
3. Lithium B-Isopinocamphey1-9-borabicyclo[3.3.1]nonyl Hydride. A New Reagent for the Asymmetric Reduction of Ketones with Remarkable Consistency  
 S. Krishnamurthy, F. Vogel, and H. C. Brown  
*J. Org. Chem.*, 42, 2534 (1977)
4. Addition Compounds of Alkali Metal Hydrides. 13. Reactions of Alkali Metal Hydrides with Trialkylboranes. Synthesis and Dissociation of Alkali Metal Trialkylborohydrides. Ethyl Ether-Organoborane as a Reversible "Solvent" for Lithium Hydride  
 H. C. Brown, A. Khuri and S. C. Kim  
*Inorg. Chem.*, 16, 2229 (1977)
5. Addition Compounds of Alkali Metal Hydrides. 14. The Reaction of Trialkylboranes with Lithium Trialkylborohydrides  
 H. C. Brown, A. Khuri and S. Krishnamurthy  
*J. Am. Chem. Soc.*, 99, 6237 (1977)
6. Addition Compounds of Alkali Metal Hydrides. 15. Steric Effects in the Reaction of Representative Trialkylboranes with Lithium and Sodium Hydrides to Form the Corresponding Trialkylborohydrides  
 H. C. Brown, S. Krishnamurthy and J. L. Hubbard  
*J. Am. Chem. Soc.*, 100, 3343 (1978).
7. Addition Compounds of Alkali Metal Hydrides. 16. Facile Reaction of Trialkylboranes with Lithium Trimethoxyaluminohydride to Form Lithium Trialkylborohydrides. Rapid and Quantitative Transfer of Hydride from Aluminum to Boron  
 H. C. Brown, S. Krishnamurthy and J. L. Hubbard  
*J. Organometal. Chem.*, 166, 271 (1979)
8. Addition Compounds of Alkali Metal Hydrides. 17. An Unusual Reaction of Trialkylboranes with Lithium Tri-t-butoxyaluminohydride in Tetrahydrofuran  
 H. C. Brown, S. Krishnamurthy, J. L. Hubbard and R. A. Coleman  
*J. Organometal. Chem.*, 166, 281 (1979)

9. An Examination of Convenient Procedures for the Conversion of Sodium Borohydride into Lithium Borohydride  
H. C. Brown and Y. M. Choi  
*Inorg. Chem.*, manuscript in preparation
10. A Convenient Procedure for the Preparation of Borane Methyl Sulfide from Various Metal Borohydrides  
H. C. Brown and Y. M. Choi  
manuscript in preparation
11. Reduction of Representative Ester to Alcohol with Lithium Borohydride, Calcium Borohydride, and Borane Methyl Sulfide  
H. C. Brown and Y. M. Choi  
manuscript in preparation
12. Addition Compounds of Alkali Metal Hydrides. Steric Effects in the Reaction of Representative Mono- and Dialkylboranes with Alkali Metal Hydrides  
H. C. Brown, C. P. Mathew and B. Singaram  
manuscript in preparation
13. Forty Years of Hydride Reduction  
H. C. Brown and S. Krishnamurthy  
*Tetrahedron*, 35, 567 (1979)
14. Boranes for Organic Reduction - A Forty Year Odyssey  
H. C. Brown and S. Krishnamurthy  
*Aldrichimica Acta*, 12, 3 (1979)